Journal of the Industrial Technology Research Institute.
Korea Maritime University. Vol. 13. 1995.

Pulsed Laser Deposition에 의한 MPB-PZT 박막의 제조

이 병 우*

Preparation of MPB-PZT Thin Films by Pulsed Laser Deposition

B. W. Lee

Abstract

Morphotropic phase boundary (MPB) PZT thin films were prepared by pulsed excimer laser irradiation of dense ceramic targets. Films were deposited with ambient oxygen pressure of 2.7-40 Pa. Substrate temperatures were varied from room temperature to 650℃. Phase formation and morphology of the films varied according to deposition conditions. Films were crystallized in situ during deposition or by post depositional heat treatment (post annealing). The ratio, perovskite to pyrochlore, was found to depend on the deposition conditions such as substrate temperature and ambient oxygen pressure. Formation of two types of pyrochlore was discussed. A PZT film formed from a target having the morphotropic phase boundary composition showed no tetragonal X-ray peak splitting. However, Raman spectroscopy suggested that this film had mixed tetragonal and rhombohedral phases, the same as the target.

1. INTRODUCTION

Ferroelectric thin films are of great interest for device applications involving actuators, pyroelectric sensors, electro-optic devices and integrated devices such as nonvolatile random access memory (RAM)[1-4]. For these applications, recent studies have focused on the deposition of the films onto semiconductor substrates[1-6].

Lead zirconate titanate ($PbZr_xTi_{1-x}O_3$, PZT), in particular, morphotropic phase boundary PZT of composition $PbZr_{0.53}Ti_{0.47}O_3$ has significant potential in such device applications. Pulsed laser deposition is a promising method for preparing multicomponent ceramic thin

* 한국해양대학교 이공대학 재료공학과

films, including ferroelectric materials, due to the low compositional deviation between target and film, and due to the relatively high deposition rate[6-8].

In pulsed laser deposition, the films can be crystallized in situ as they are deposited on hot substrate or by post annealing for the films deposited amorphously on lower temperature substrate. The phase formation of films can be altered by deposition conditions (i.e. substrate temperature, ambient oxygen pressure) and the post annealing where applicable.

This paper describes the deposition conditions and the effect of preparation methods on the phase formation of morphotropic phase boundary (designated as MPB) PZT thin films. This study also includes a Raman spectroscopy examination of the coexistence of tetragonal and rhombohedral phases in PZT films formed from a target of MPB composition.

2. EXPERIMENTAL PROCEDURE

Cearmic Target of $PbZr_{0.53}Ti_{0.47}O_3$ (MPB-PZT) composition having tetragonal and rhombohedral both phases were prepared by conventional firing of oxides at 1250℃ in a lead vapor containing atmosphere. The targets contained 10 mol% excess PbO to compensate for lead loss during the high temperature (>600℃) deposition or post annealing. The geometry of the deposition apparatus is shown in Fig. 1. The apparatus is placed in a cylindrical vaccum chamber which is equipped with multiple ports. The laser (ArF) beam was brought into the chamber and onto the target at an incidence angle of ~35° through a windowed port. During deposition, a luminous plume was produced, the axis of which was perpendicular to the target surface. Targets were continuously rotated while translating back and forth along one axis, in order to focus each pulse on a different area of the target and uniformly vaporize the target. The ArF excimer laser was operated at 193 nm, with a repetition rate of 10 Hz, a nominal pulse width of 23 ns, and a fluence of ~16 J/cm^2.

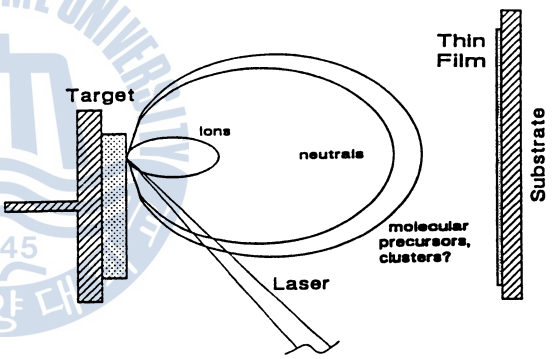

Fig.1. Geometry of the deposition apparatus.

Films were deposited onto Pt-coated Si single crystal wafers. The substrate was heated by passing a dc current through the substrate itself. Substrate temperature ranged from room temperature (R.T.) to 650℃ and ambient oxygen pressure (P_{O2}) was 2.7-40 Pa.

Temperature was monitored with a K-type thermocouple attached to the back of the substrate. The target-to-substrate distance was varied from 1.5 to 4 cm, depending upon P_{O2}, because plume diameter was reduced with increasing P_{O2}. The growth rate of the films was 16-25 nm/min. The thickness of the films was 0.7-1.5 μm as measured by profilometry. For amorphous films deposited below the crystallization temperature, post annealing was conducted in air from the deposition temperature to 650℃.

The morphology and the composition of the films were studied using a scanning electron microscope (SEM) and an energy dispersive X-ray (EDX) respectively. Phase identification and crystallographic texture were analyzed by powder X-ray diffractometer (XRD) using Cu-Kα radiation and a computer-controlled theta/two-theta diffractometer with two-theta compensating slit and at a step size of 0.03° and a counting interval of 1.7 sec. The phase identification was also carried out by Raman spectroscopy.

3. RESULTS AND DISCUSSION

The PZT films prepared were produced with predominantly amorphous, pyrochlore, perovskite, or mixed-phase content, the same results as previously reported modified-$PbTiO_3$ films[9]. Crystalline phases were obtained by in situ crystallization at deposition temperature 〉 450℃ and the perovskite phase, which was desirable ferroelectric phase, increased with increasing P_{O2} and increasing deposition temperature up to 40 Pa and 650℃ respectively.

Post annealed films showed two different crystallization routes, i.e. direct to perovskite and indirect to perovskite at the expense of existing pyrochlore. Amorphous film deposited at P_{O2}=13 Pa, R.T. showed the both direct and indirect crystallization routes while the films deposited at P_{O2}=40 Pa, R.T. showed almost direct crystallization to perovskite. From the results, it is suggested that the phase formation (i.e. perovskite, pyrochlore and perovskite to pyrochlore ratio) of post annealed films deposited below crystallization temperature was mainly influenced by depositional P_{O2}. In both cases of low and high P_{O2}, the pyrochlore phase, which is undesirable paraelectric phase, decreased with increasing annealing temperature and at 650℃, single phase perovskite films were obtained. These results showed that the pyrochlore phase formed in the post annealing process was metastable; the XRD pattern of this phase matched the oxygen deficient lead zirconate titanate indexed as cubic.

Pyrochlore is known as a metastable oxygen deficient phase formed at relatively low temperature, below 500℃[10,11], in agreement with the post annealing results. In the in situ

crystallization, however, the pyrochlore formed above 500℃ and it was even the dominant phase in low oxygen pressure depositions[9]. This type of high temperature pyrochlore phase, once formed, could not be transformed to perovskite easily by subsequent heat treatment. EDX analysis showed that the pyrochlore formed at high temperature is lead deficient as well as oxygen deficient. The lead deficient pyrochlore may be the result of lead re-evaporation at film surface due to the hot substrate[12]. Lead deficient pyrochlore has been repoted[13,14], and it seems to be thermodynamically stable under some conditions, where the perovskite phase becomes unstable due to lead loss.

Perovskite single phase was obtained by in situ crystallization (e.g. at P_{O2}=40 Pa, 650℃) or post annealing at 650℃ for films deposited at below crystallization temperature. Since the temperature readings during deposition were only approximate, and the post annealed films had different crystallization routes, determining the exact crystallization temperature was difficult. Based on the previous study[15], the onset of crystallization temperature is estimated at around 450℃.

Fig. 2 shows the morphology of the films deposited at different conditions. Fig. 2 (a) shows a film deposited and crystallized in situ at P_{O2}=40 Pa, 650℃. Above the crystallization onset temperature (〉 450℃), nucleation and growth of the film took place during deposition and the film had well-defined crystallites with shaped edges. A marked difference of a dome-shaped surface is observed in a film (Fig. 2 (b)) post annealed at 650℃, which was originally an amorphous film deposited P_{O2}=40 Pa, 300℃.

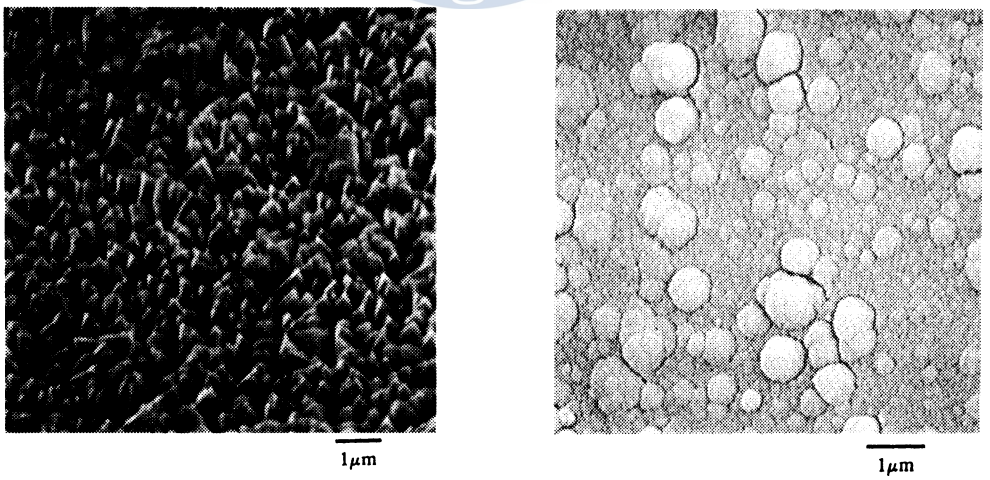

Fig. 2. SEM micrographs of the PZT films:(a) deposited at P_{O2}=40 Pa, 650℃ (b) deposited at P_{O2}=40 Pa, 300℃ then post annealed at 650℃.

The structure of PZT films near the MPB composition was ambiguous because XRD pattern showed lack of tetragonal peak splitting such as (200) and (002), and only indexed cubic or rhombohedral as shown in Fig. 3 (b). While the XRD pattern of the sintered ceramic near the MPB shows tetragonal and rhombohedral peaks simultaneously as shown in Fig. 3 (a). The rhombohedral (200) peak is located between the tetragonal (200) and (002) peaks.

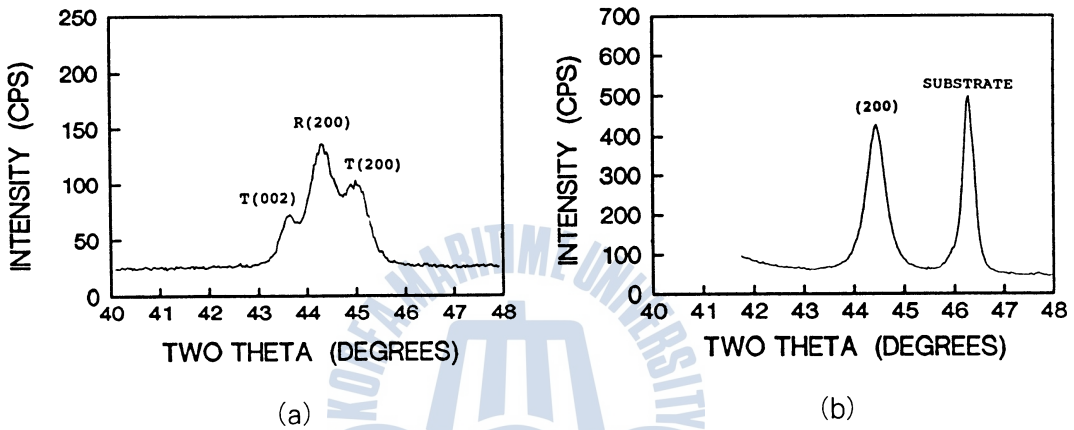

Fig. 3. XRD patterns of MPB-PZT (a) target , (b) film.made from the target

In PZT ceramics, Raman spectra can reflect structural information[16]. Fig. 4 shows Raman spectra of a tetragonal $PbZr_{0.4}Ti_{0.6}O_3$ and a rhombohedral $PbZr_{0.8}Ti_{0.2}O_3$ (PZT) ceramic and Fig.5 (a) shows Raman spectra of a MPB-PZT ceramic target. The spectra of MPB-PZT target shows convolution of both tetragonal and rhombohedral. Raman spectra (Fig. 5 (b)) of the film made by MPB-PZT ceramic target also shows almost the same pattern as shown in its target. From these results, it is suggested that the film has tetragonal and rhombohedral mixed structures.

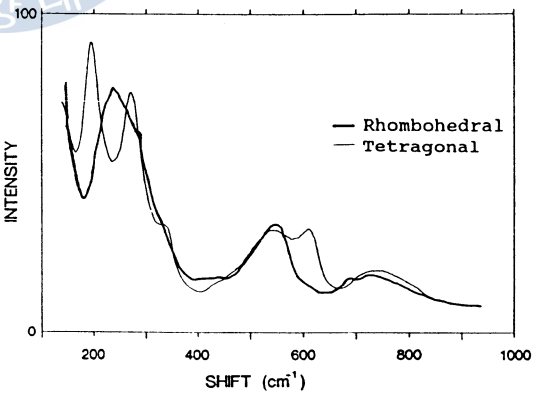

Fig. 4. Raman spectra of tetragonal-PZT ($PbZr_{0.4}Ti_{0.6}O_3$) and rhombohedra-PZT ($PbZr_{0.8}Ti_{0.2}O_3$) ceramic.

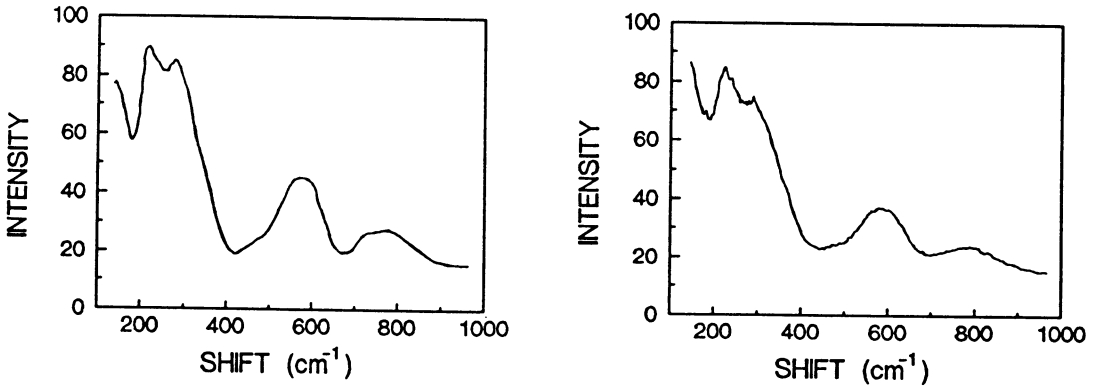

Fig. 5. Raman spectra of MPB-PZT (a) target , (b) film.

4. CONCLUSION

Thin films of MPB-PZT have been deposited on platinum coated silicon wafer using an ArF excimer laser. Unlike the pyrochlore phase formed during post annealing, the pyrochlore phase formed by in situ crystallization at relative high temperature was lead deficient as well as oxygen deficient, and rather stable. Ferroelectric perovskite films without pyrochlore were obtained by in situ crystallization at P_{O2}=40 Pa, 650℃ as well as by post annealing at 650℃ for amorphously deposited films. Films crystallized in situ during deposition have shown well-defined crystallites with shaped edges, while the films prepared by post annealing have shown a dome-shaped surface. Although X-ray diffraction pattern of MPB-PZT film showed no tetragonal peak splitting (e.g. (002) and (200)) which was shown in the pattern of MPB-PZT ceramic target, Raman spectra analysis suggested that the film had mixed tetragonal and rhombohedral phases, the same as the target.

REFERENCES

1. W.A. Geideman, IEEE, Trans. Ultrasonics, Ferroelectrics, and Frequency Control, 38(6), 704-711 (1991).
2. M. Okuyama and Y. Hamakawa, Ferroelectrics, 63, 243-256 (1985).
3. C.A. Paz de Araujo, L.D. McMillan, B.M. Melnick, J.D. Cuchiaro, and J.F. Scott, Ferroelectrics, 104, 241-256 (1990).
4. K. Uchino, M. Aizawa and S. Nomura, Ferroelectrics, 64, 199-208 (1985).
5. S.K. Dey and R. Zuleeg, Ferroelectrics, 108, 37-46 (1990).
6. K.L. Saenger, R.A. Roy, K.F. Etzold, and J.J. Cuomo, Mat. Res. Soc. Proc., 200, 115-120 (1990).

7. G.A. Petersen, Jr. and J.R. McNeil, Thin Solid Films, 220, 87-91 (1992).
8. S. Otsubo, T. Maeda, T. Minamikawa, Y. Yonezawa, A. Morimoto, and T. Shimizu, Jpn, Appl. Phys., 29(1) L133-L136 (1990).
9. B.W. Lee, H.M. Lee, L.P. Cook, P.S. Schenck, A. Paul, C.K. Chiang, and P.S. Brody, Mat. Res. Soc. Symp. Proc., 285, 403-407 (1993).
10. K. Iijima, Y. Tomita, R. Takayama, and I. Ueda, J. Appl. Phys., 60, 361-367 (1986).
11. M. Ishida, H. Matsunami, and T. Tanaka, J. Appl. Phys., 48, 951-953 (1977).
12. K.S. Grabowski, J.S. Horwitz, and D.B. Chrisey, Ferroelectrics, 116, 19-33 (1991).
13. A.H. Carim, B.A. Tuttle, D.H. Doughty, and S.L. Martinez, J. Am. Ceram. Soc., 74, 1455-1458 (1991).
14. C.V.R. Vasant Kumar, R. Pascual, and M. Sayer, J. Appl. Phys., 71, 864-874 (1992).
15. L.P. Cook, M.D. Vaudin, P.K. Schenck, W. Wong-Ng, C.K. Chiang, and P.S. Brody, Mat. Res. Soc. Symp. Proc., 202-227 (1991).
16. G. Burns and B.A. Scott, Phys. Rev. Lett., 26, 1191-1194 (1970).